

INDUSTRIAL CARTRIDGE AND CANISTER EVALUATIONS

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Current bench tests for organic vapor respirator cartridge and canister sorbents require successful performance against airborne concentrations of carbon tetrachloride for NIOSH approval. However, these tests are not sufficiently indicative of the performance of respirator sorbents against the wide variety of organic vapors that may be encountered in an industrial environment. Consequently, at Haskell Laboratory for Toxicology and Industrial Medicine, we have set up a respirator cartridge and canister evaluation program to determine the breakthrough time and service-life of these protective devices against hazardous chemical vapors or gases that may be encountered at our plant locations. The vapors or gases selected for testing are suggested by industrial hygienists who have visited the plant on surveys and find that while corrective action is being taken to control or eliminate exposures, temporary protective devices such as respirator cartridges or canisters are needed. This is particularly true for hazardous vapors that either have poor warning properties or for which there is concern about the possible toxicity. Additional factors at the plant location such as relative humidity and mixed atmospheres of vapors also may influence the performance of these devices, hence, cartridge or canister testing is proposed.

Our cartridge and canister evaluation program is modelled after the system designed by Gary Nelson of the Lawrence Livermore Laboratory, University of California, reported in a series of articles in the American Industrial Hygiene Association Journal. (1-8) challenge upstream airborne concentrations are generated at current Threshold Limit Values, at 50% relative humidity, at breathing rates of 60 liters per minute and passed through selected cartridges or canisters until breakthrough occurs downstream on the breathing side. Both upstream and downstream concentrations are monitored continuously by analytical methods specific and sensitive to the vapor concentration. Three cartridge pairs or individual canisters are evaluated per test condition. Both relative humidity and flow rate are also monitored continuously for the duration of the test. All tests are run until a 10% breakthrough concentration is found downstream.

A typical setup is shown in Figure 1. Houseline air is monitored through a calibrated flowmeter, a complete saturation humidifying system, consisting of a heating element, flask of water and a condenser, then through the test cartridge or canister to a filter trap and dry test meter downstream. The vapor or gas is introduced into the air flow by an appropriate generation system, upstream from the cartridge or canister, where it can be monitored, mixed and diluted to the desired test concentration. A three-way Teflon valve located just upstream from the cartridge or canister allows for by-passing the cartridge or canister until upstream test conditions and concentration have equilibrated. Both upstream and downstream sampling ports allow for continuous monitoring of the concentration by appropriate sampling and analytical techniques. Continuous monitoring of the relative humidity and temperature is accomplished with a Humi-Temp Controller from Phys-Chemical Research Corporation, New York. Constant humidity solutions are used to calibrate this instrument at the desired test humidity and temperature.

One of the nice features of this set up is the flexibility it permits for inter-changing different types of cartridges or canisters. By simply substituting a stainless steel cartridge holder in place of a canister different types and sizes of cartridges can be tested. This system can also be set up conveniently in a laboratory hood where peripheral sampling and analytical devices easily can be attached. The set up as **shown** has been used for the evaluation of about **fifteen** different organic vapors at our laboratory. Recently, two similar systems have successfully been set up at two **other** plant locations in our company.

Results from **these** evaluations have shown that there are three major factors that influence breakthrough times. They are concentration, relative humidity and amount of sorbent. Two other **contributing** factors relating to the physical and chemical properties of the vapor or gas are the boiling point and reactive groups. Examples of how each of these factors influence **breakthrough** times can be seen from cartridge and canister evaluations conducted with acrylonitrile and acrolein, two of the fifteen organic vapors tested with this system.

Acrylonitrile and acrolein both have similar chemical structures, molecular weights and odor thresholds greater than their Threshold Limit Values (**TLV's**). Their current permissible exposure limits are 2 ppm and 0.1 ppm respectively. Both vapors have disagreeable odors, particularly acrolein. Acrylonitrile is now classified as a suspect **carcinogen** in man and therefore no exposure, as detected by the most sensitive method is permitted. Table I shows the physical and chemical properties of both compounds. Note that except for a difference of 25° in boiling points and different reactive groups both compounds are quite similar.

Results of the evaluations of cartridges and canisters tested separately against both acrylonitrile and acrolein vapors are shown in Tables **II-IV**. All cartridges and canisters tested were from Mine Safety and Appliance (MSA) and were specified for use with organic vapors. There were three different sizes of **canisters**, a chin-type, industrial size and **VCM-SS** type, each having increasing amounts **of** charcoal. They were all evaluated in triplicate as received from the manufacturer at a constant flow rate of 60 liters per minute and at ambient room temperature. Various test conditions of concentration, relative humidity and amount of sorbent were used **to** determine performance.

Upstream airborne concentrations of acrolein and acrylonitrile were generated by a syringe injection **pump** that continuously introduced liquid droplets **into** the air flow. Acrolein was analyzed by the **spectrophotometric** method reported in the NIOSH Manual of Analytical **Methods** (9), while acrylonitrile was analyzed by a gas **chromatographic** method developed at our laboratory. Breakthrough was determined when an **amount of acrylonitrile** and acrolein equivalent to 10% of the upstream concentration was found downstream on the breathing side.

TABLE 1

	<u>Acrylonitrile</u>	<u>Acrolein</u>
Structure	$\text{CH}_2 - \overset{\text{H}}{\underset{ }{\text{C}}} - \text{CN}$	$\text{CH}_2 - \overset{\text{H}}{\underset{ }{\text{C}}} - \text{CHO}$
Molecular Weight	53	56
Boiling Point	77°C	53°C
Specific Gravity	0.81	0.84
Threshold Limit Value	2	0.1
Odor Threshold	21	0.2

TABLE II

<u>Vapor</u>	<u>Protective Device</u>	<u>Amount of Adsorbent</u> gms	<u>Analytical Conc.</u> ppm	<u>Breakthrough Time</u> hours
Acrolein	MSA, organic vapor cartridge	50	1 (1)	0.17
	MSA, industrial canister	420	4	0.17
Acrylonitrile	MSA, organic vapor cartridge	50	250 (2)	3
	MSA, industrial canister	420	10	87
	MSA, industrial canister	420	139	30
	MSA, industrial canister	420	1228	6

(1) **Minimum Detectable Limit** Acrolein 0.01 ppm (v/v)

(2) **Minimum Detectable Limit** Acrylonitrile 0.7 ppm (v/v)

TABLE III

<u>Vapor</u>	<u>Protective Device</u>	<u>Amount of Adsorbent gms</u>	<u>%RH</u>	<u>Analytical Conc. ppm</u>	<u>Breakthrough Time hours</u>
Acrylonitrile	MSA, industrial canister	420	7	10	94
	N	420	50	10	87
	N	420	90	10	16

TABLE IV

<u>Vapor</u>	<u>Protective Device</u>	<u>Amount of Adsorbent gms</u>	<u>Analytical Conc . ppm</u>	<u>Breakthrough Time hours</u>
Acrylonitrile	MSA, canister	220	10	64
	MSA industrial	420	10	87
	MSA VCM-SS	760	20	158

The data reported in Table II illustrate that even **though** acrylonitrile and acrolein both have **similar** chemical structures, and **molecular** weights they do not behave the same when adsorbed on charcoal **sorbent**. Apparently, the aldehyde functional group on acrolein is not adsorbed readily by charcoal and, **therefore**, no matter how **much** charcoal is present it passes right through in about 10 minutes. Acrylonitrile, on the other hand, with the nitrile group attached, has a greater affinity for charcoal and is retained, resulting in a longer breakthrough time. Note also that the breakthrough time decreases with increasing concentration of acrylonitrile, indicating the inverse relationship between concentration and adsorption capacity of charcoal sorbent.

Results of the effect of relative humidity on the breakthrough time of acrylonitrile are shown in Table III. About a five fold decrease in breakthrough time was found at a analytical concentration of 10 **ppm** and 90% R.H., compared to that measured at 50% R.H. Figure 2, shows a plot of breakthrough time vs. relative humidities.

In Table IV results of the evaluation of chin type canisters, industrial size and one large type **VCM-SS** canister against acrylonitrile vapor **demonstrate** that breakthrough times are **proportional** to the **amount** of charcoal present in the canisters. The chin-type canisters had one half the amount of charcoal found in the industrial size canister while the VCM-SS canister had almost two times the amount of carbon sorbent. The breakthrough times found for the respective canisters were approximately two thirds and two times the breakthrough time observed in the industrial size canister. Figure 3, shows a plot of the breakthrough times of the three types of canisters vs. the amount of charcoal.

Results of these evaluations with acrylonitrile and acrolein illustrate that breakthrough times are unpredictable for different types of compounds and that by measuring breakthrough times at conditions that may be encountered at plant locations a better estimate of the protective capacity of cartridges **and** canisters can be obtained. This information can be utilized by our industrial hygienists in selecting and **recommending** cartridges or canisters with established service lives and performance data obtained experimentally from our evaluation **program**.

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FIGURE 1.

[Fran Henry, et al (AIHA Journal, 40, 1017-1022, 1979), with permission]

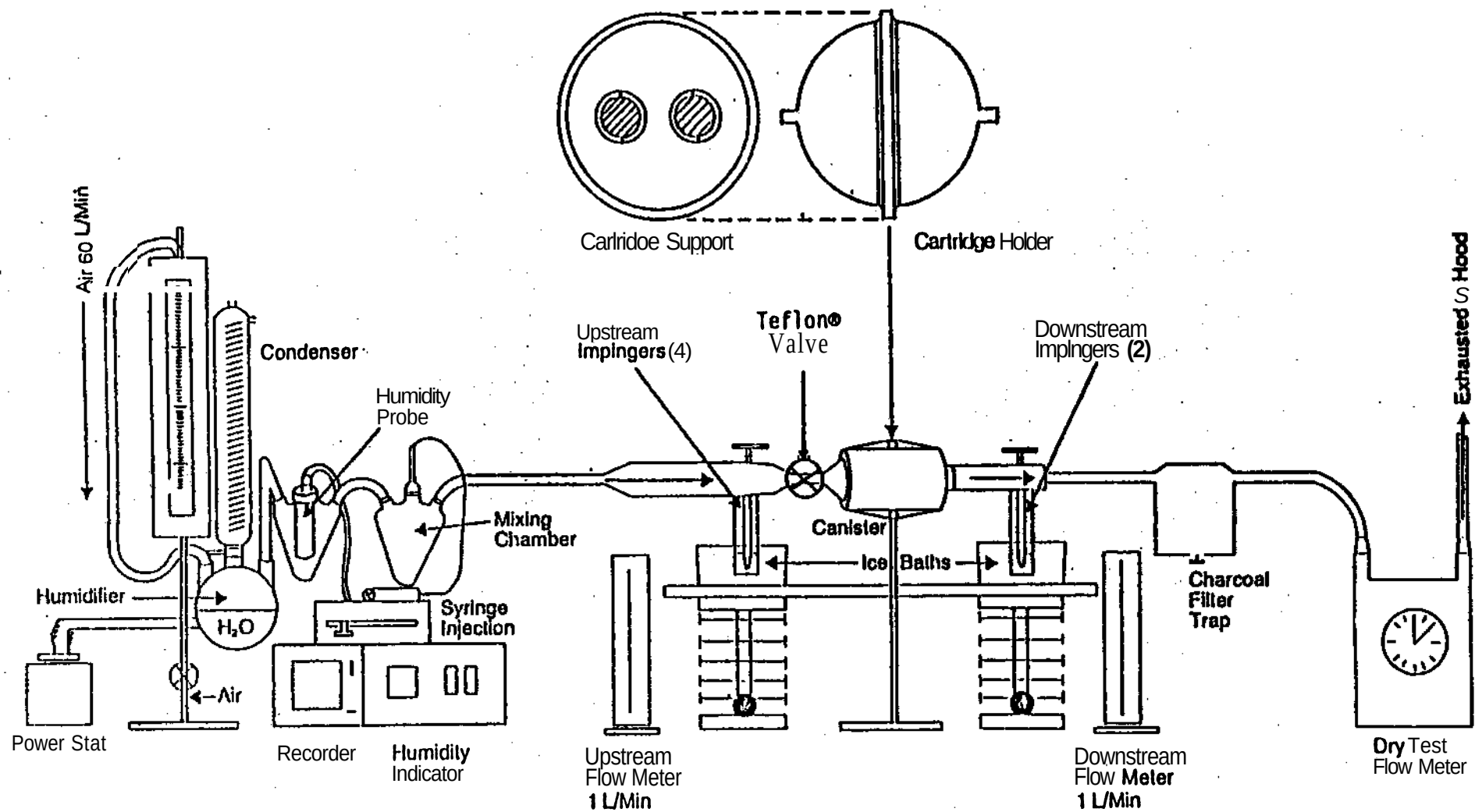


Figure 2

[Fran Henry, et al (AIHA Journal, 40, 1017-1022, 1979), with permission]
BREAKTHROUGH TIME VS. RELATIVE HUMIDITY

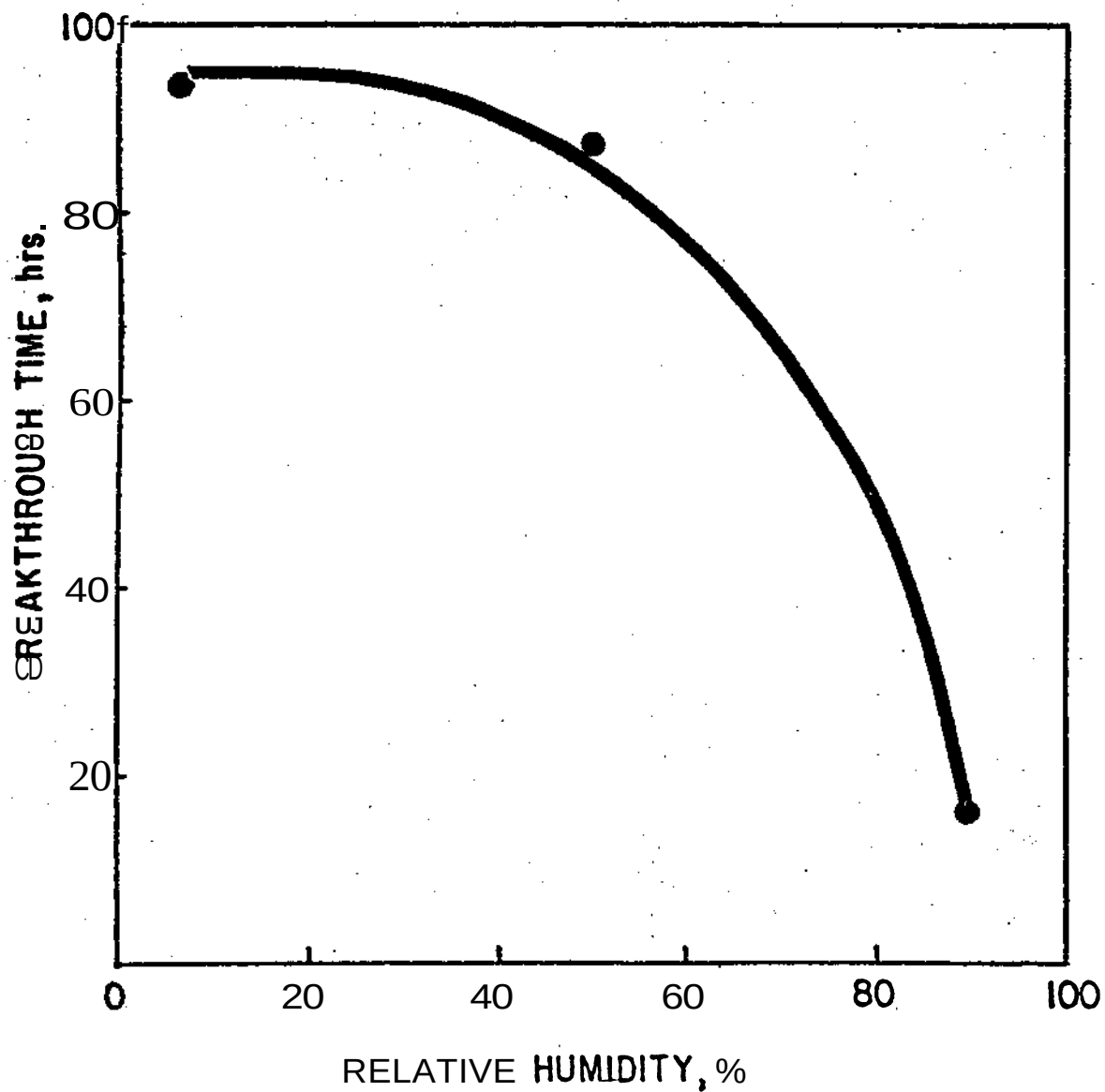
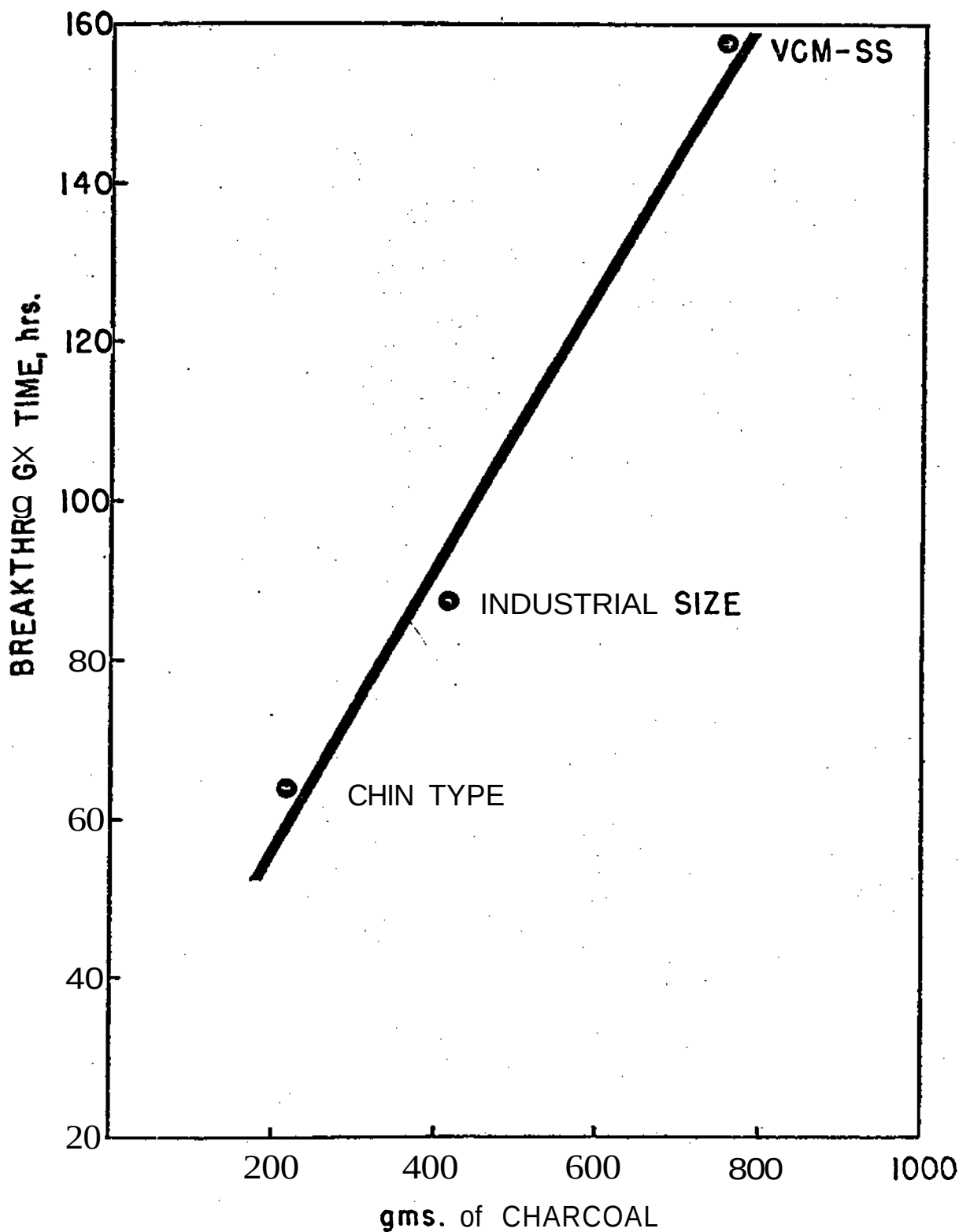


Figure 3

BREAKTHROUGH TIME VS. GRAMS CHARCOAL

[From Henry, et al, (AIHA Journal, 40, 1017-1022, 1979), with permission]



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